PATENT
Attorney Docket No. 225101
Client Reference No. GN 02128-THSTAB5

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Geuens et al.

Application No. Unassigned

Art Unit: Unassigned

Examiner: Unassigned

Filed: November 13, 2003

For: STABILIZERS FOR USE IN SUBSTANTIALLY LIGHT-INSENSITIVE THERMOGRAPHIC RECORDING MATERIALS

CLAIM OF PRIORITY

Mail Stop Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

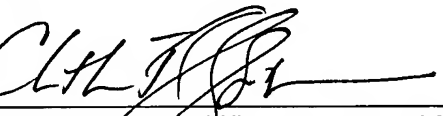
Dear Sir:

In accordance with the provisions of 35 USC 119, Applicants claim the priority of the following application:

Application No. 02102586.1, filed in Europe on November 14, 2002.

A certified copy of the above-listed priority document is enclosed.

Respectfully submitted,



Christopher T. Griffith, Reg. No. 33,392
LEYDIG, VOIT & MAYER, LTD.
Two Prudential Plaza, Suite 4900
180 North Stetson
Chicago, Illinois 60601-6780
Telephone: (312) 616-5600
Facsimile: (312) 616-5700

Date: November 13, 2003

GN02128

Europäisches Patentamt	European Patent Office	Office européen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.	The attached documents are exact copies of the European patent application described on the following page, as originally filed.	Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

02102586.1

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 02102586.1
Demande no:

Anmeldetag:
Date of filing: 14.11.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

AGFA-GEVAERT
Septestraat 27
2640 Mortsel
BELGIQUE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Stabilizers for use in substantially light-insensitive thermographic recording materials

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B41M/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

DESCRIPTION

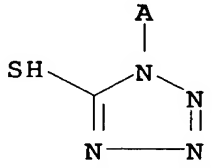
FIELD OF THE INVENTION

The present invention concerns stabilizers for use in substantially light-insensitive thermographic recording materials.

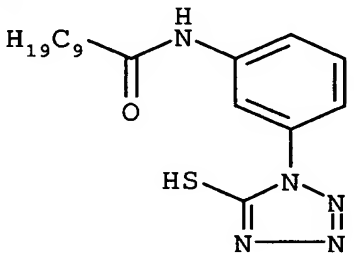
BACKGROUND OF THE INVENTION

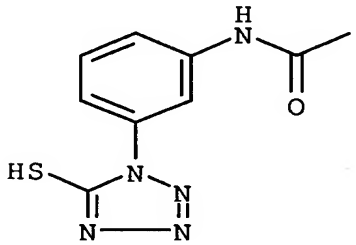
Thermography is an image-forming process including a heating step and hence includes photothermography in which the image-forming process includes image-wise exposure and direct thermal processes in which the image-forming process includes an image-wise heating step. In direct thermal printing a visible image pattern is produced by image-wise heating of a recording material.

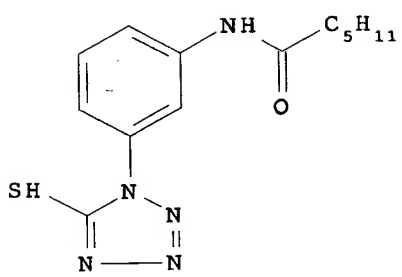
EP-A 0 713 133 discloses a thermal imaging system consisting of (i) a donor element comprising on a support a donor layer containing a binder and a thermotransferable reducing agent capable of reducing a silver source to metallic silver and (ii) a receiving element comprising on a support a receiving layer comprising a silver source, capable of being reduced by means of heat in the presence of a reducing agent, a binder and a stabiliser selected from the group consisting of benzotriazoles, heterocyclic mercaptanes, sulphinic acids, 1,3,4-triazo-indinolines, 1,3-dinitroaryl compounds, 1,2,3-triazoles, phthalic acids and phthalic acid derivatives. EP-A 0 713 133 discloses that preferred heterocyclic mercaptanes are mercaptotetrazoles corresponding to the following general formula (C):

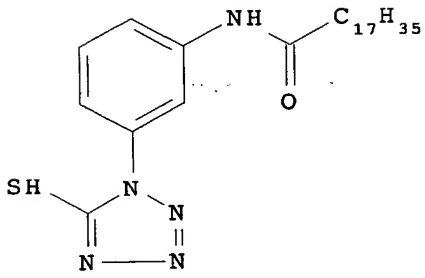


and discloses the following 1-phenyl-5-mercapto-tetrazole compounds:

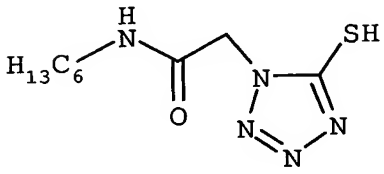


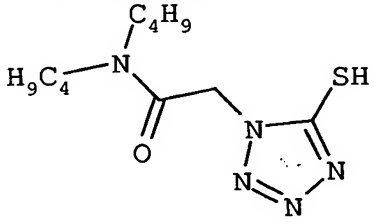




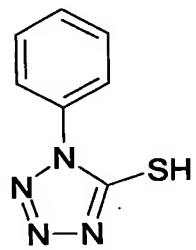


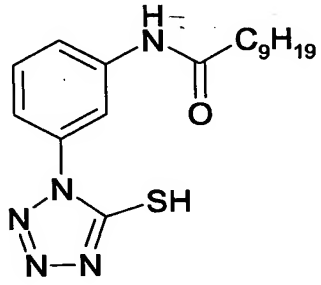
and the following 1-(5-mercapto-1-tetrazolyl)-acetyl compounds:

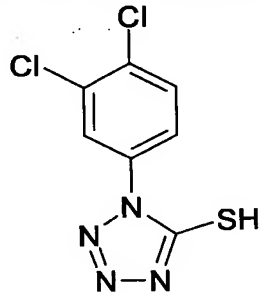




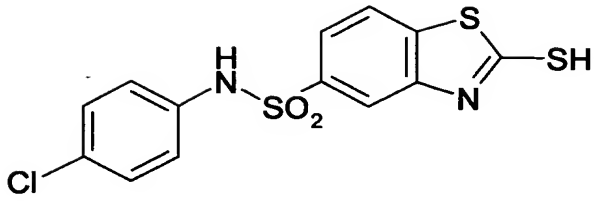
EP-A 0 901 040 discloses a substantially light-insensitive monosheet recording material comprising a support and a thermosensitive element containing a substantially light-insensitive organic silver salt, an organic reducing agent therefor in thermal working relationship therewith and a binder, characterized in that said thermosensitive element further contains an unsaturated carbocyclic or heterocyclic stabilizer compound substituted with a -SA group where A is hydrogen, a counterion to compensate the negative charge of the thiolate group or a group forming a symmetrical or an asymmetrical disulfide and said recording material is capable of producing prints with a numerical gradation value defined as the quotient of the fraction (2.5 - 0.1)/($E_{2.5}$ - $E_{0.1}$) greater than 2.3, where $E_{2.5}$ is the energy in Joule applied in a dot area of 87 µm x 87 µm of the imaging layer that produces an optical density value of 2.5, and $E_{0.1}$ is the energy in Joule applied in a dot area of the imaging layer material that produces an optical density value of 0.1. EP-A 0 901 040 discloses the following 1-phenyl-5-mercapto-tetrazole compounds:







and the following 2-mercapto-benzothiazole compound:



WO 94/16361 discloses a multilayer heat-sensitive material which comprises: a color-forming layer comprising: a color-forming amount of finely divided, solid colorless noble metal or iron salt of an organic acid distributed in a carrier composition; a color-developing amount of a cyclic or aromatic organic reducing agent, which at thermal copy and printing temperatures is capable of a color-forming reaction with the noble metal or iron salt; and an image-toning agent; characterized in that (a) the carrier composition comprises a substantially water-soluble polymeric carrier and a dispersing agent for the noble metal or iron salt and (b) the material comprises a protective overcoating layer for the color-forming layer. Furthermore, WO 94/16361 discloses that suitable antifoggants are well-known photographic anti-foggants such as mercaptobenzotriazole, chromate, oxalate, citrate, carbonate, benzotriazole (BZT), 5-methylbenzotriazole, 5,6-dimethylbenzotriazole, 5-bromobenzotriazole, 5-chlorobenzotriazole, 5-nitro-benzotriazole, 4-nitro-6-chlorobenzotriazole, 5-nitro-6-chlorobenzotriazole, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, benzimidazole, 2-methylbenz-imidazole, 5-nitrobenzimidazole, 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptothiazoline, 2-mercapto-4-methyl-6,6'-dimethylpyrimidine, 1-ethyl-2-mercapto-5-amino-1,3,4-triazole, 1-ethyl-5-mercapto-1,2,3,4-tetrazole, 2,5-dimercapto-1,3,4-thiodiazole, 2-mercapto-5-aminothiodiazole, dimethyldithiocarbamate, and diethyldithiocarbamate.

WO 96/10213 discloses a thermographic imaging element comprising a substrate having coated on at least one surface thereof a thermographic imaging system comprising at least one layer comprising light-insensitive organic silver salt; reducing agent for silver ion; binder; toner; and a dye which absorbs radiation in the wavelength range of 750-1100 nm, wherein said at least one layer comprising said light-insensitive organic silver salt forms an image density greater than about 1.0 when exposed to 0.10 - 2.0 joules/cm^2 of said radiation in 0.20 to 200 microseconds. WO 96/10213 does not disclose a stabilizer against the influence of light, but mentions the optional incorporation of benzotriazole in the thermographic imaging element, but only exemplifies the incorporation of benzotriazole.

Substantially light-insensitive thermographic recording materials contain the imaging-forming components both before and after image formation and unwanted image-forming must be hindered both during storage prior to printing and in prints exposed to light on light-boxes e.g. during examination by radiologists. Furthermore, such stabilization must take place without adverse effects upon the image quality particularly the image tone. Thermographic printers are being introduced with ever higher throughputs, which require thermographic recording materials able to provide stabilization without an adverse effect on the image quality at such faster throughputs. There is therefore a need for stabilizers which fulfil these requirements.

ASPECTS OF THE INVENTION

It is therefore an aspect of the present invention to provide stabilizers for use in substantially light-insensitive thermographic recording materials suitable for use in high throughput thermographic printers without adverse effect on the image tone.

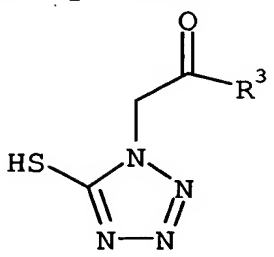
Further aspects and advantages of the invention will become apparent from the description hereinafter.

SUMMARY OF THE INVENTION

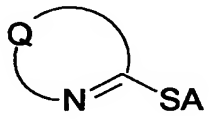
It has been surprisingly found that specific types of 5-mercapto-tetrazole compounds provide effective stabilization in substantially light-insensitive thermographic recording materials suitable for use in high throughput thermographic printers without an adverse effect on the image tone as characterized by CIELAB a* and b* values. The L*, a* and b* CIELAB-values were determined by spectrophotometric measurements according to ASTM Norm E179-90 in a R(45/0) geometry with evaluation according to ASTM Norm E308-90.

Aspects of the present invention are realized with a substantially light-insensitive black and white monosheet thermographic recording material comprising a support and a thermosensitive element, the thermosensitive element containing a substantially light-insensitive organic silver salt, an organic reducing agent therefor in thermal working relationship therewith, a binder and at least one stabilizer selected from the group consisting of 1-phenyl-5-mercaptotetrazole compounds in which the phenyl group is substituted with a substituent containing an

optionally substituted aryl group, 1-(5-mercapto-1-tetrazolyl)-acetyl compounds represented by formula (III):

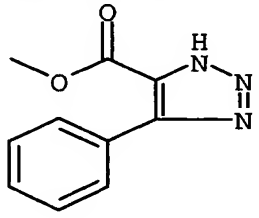


wherein R^3 is $-NR^4R^5$, $-OR^6$ or an optionally substituted aryl or heteroaryl group; R^4 is hydrogen or an optionally substituted alkyl, aryl or heteroaryl group; R^5 is an optionally substituted aryl or heteroaryl group; and R^6 is an optionally substituted aryl group; compounds with two or more groups represented by formula (IV):



(IV)

where Q comprises the necessary atoms to form a 5- or 6-membered unsaturated heterocyclic ring, A is hydrogen, a counterion to compensate the negative charge of the thiolate group or two or more A groups provide a linking group between the two or more groups represented by formula (IV); 2-mercapto-benzothiazole compounds substituted by an alkyl, an aryl, an alkoxy, a nitro, a cyano or an acyl group or a halogen atom; and



Preferred embodiments of the present invention are disclosed in the detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

The term alkyl means all variants possible for each number of carbon atoms in the alkyl group i.e. for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and

tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethylpropyl and 2-methyl-butyl etc.

The term acyl group as used in disclosing the present invention means -(C=O)-aryl and -(C=O)-alkyl groups.

The L*, a* and b* CIELAB-values are defined in ASTM Norm E179-90 in a R(45/0) geometry with evaluation according to ASTM Norm E308-90.

Substantially light-insensitive means not intentionally light sensitive.

Heating in association with the expression a substantially water-free condition as used herein, means heating at a temperature of 80 to 250°C. The term "substantially water-free condition" as used herein means that the reaction system is approximately in equilibrium with water in the air, and water for inducing or promoting the reaction is not particularly or positively supplied from the exterior to the element. Such a condition is described in T.H. James, "The Theory of the Photographic Process", Fourth Edition, Macmillan 1977, page 374.

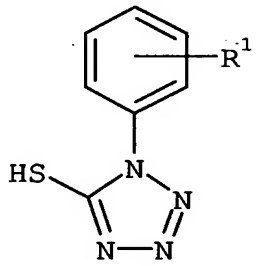
Thermosensitive element

The term thermosensitive element as used herein is that element which contains all the ingredients which contribute to image formation. According to the present invention, the thermosensitive element contains one or more substantially light-insensitive organic silver salts, one or more reducing agents therefor in thermal working relationship therewith and a binder. The element may comprise a layer system in which the above-mentioned ingredients may be dispersed in different layers, with the proviso that the substantially light-insensitive organic silver salts are in reactive association with the reducing agents i.e. during the thermal development process the reducing agent must be present in such a way that it is able to diffuse to the particles of substantially light-insensitive organic silver salt so that reduction to silver can occur. Such materials include the possibility of one or more substantially light-insensitive organic silver salts and/or one of more organic reducing agents therefor being encapsulated in heat-responsive microcapsules, such as disclosed in EP-A 0 736 799 herein incorporated by reference.

1-phenyl-5-mercaptotetrazole compounds

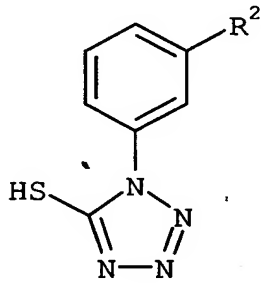
The substantially light-insensitive thermographic recording material of the present invention can contain at least one 1-phenyl-5-mercaptotetrazole compound in which the phenyl group is substituted with a substituent containing an optionally substituted aryl group.

According to a first embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the 1-phenyl-5-mercaptotetrazole compound in which the phenyl group is substituted with a substituent containing an optionally substituted aryl group is represented by formula (I):



wherein R^1 is -NH-(C=O)-Ar, -NH-(C=O)-NH-Ar, -NH-(C=O)-O-Ar, -O-(C=O)-NH-Ar, -(C=O)-NH-Ar, -NH-SO_2-Ar, -O-(C=O)-Ar, -O-(C=O)-O-Ar, -(C=O)-Ar, -(C=O)-O-Ar, -SO_2-Ar, -SO_2-NH-Ar, or -Ar; and Ar is an optionally substituted aryl or heteroaryl group.

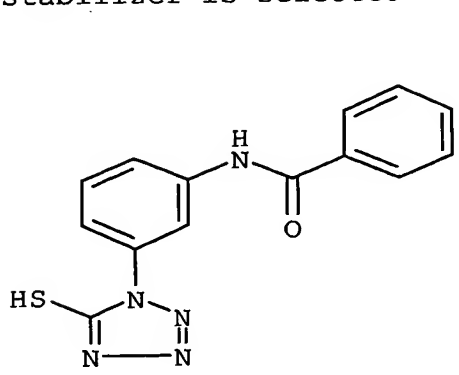
According to a second embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the 1-phenyl-5-mercaptotetrazole compound in which the phenyl group is substituted with a substituent containing an optionally substituted aryl group is represented by formula (II):

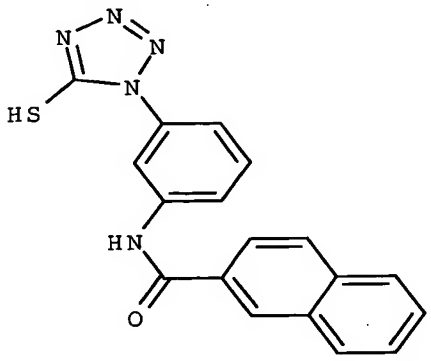


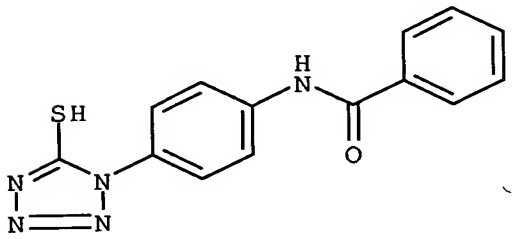
wherein R^2 is -NH-(C=O)-Ar, -NH-(C=O)-NH-Ar, -NH-(C=O)-O-Ar, -O-(C=O)-NH-Ar, -(C=O)-NH-Ar, -NH-SO_2-Ar, -O-(C=O)-Ar, -O-(C=O)-O-Ar, -(C=O)-Ar, -(C=O)-O-Ar, -SO_2-Ar, -SO_2-NH-Ar, or -Ar; and Ar is an optionally substituted aryl or heteroaryl group.

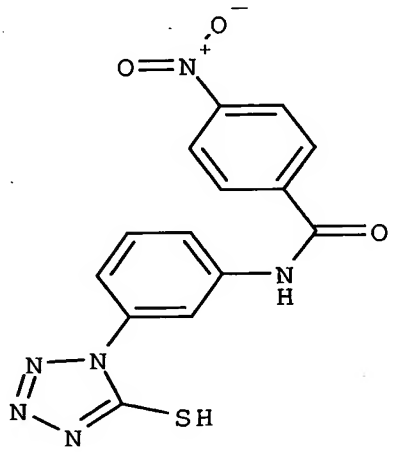
According to a third embodiment of the substantially light-insensitive black and white monosheet thermographic recording

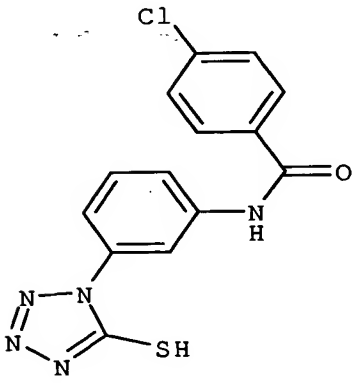
material, according to the present invention, the at least one stabilizer is selected from the group consisting of:

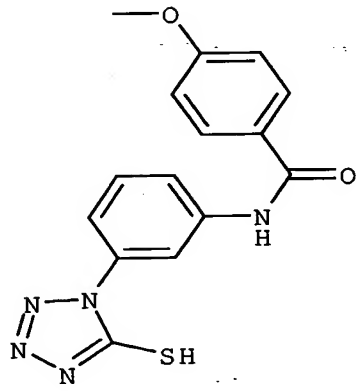


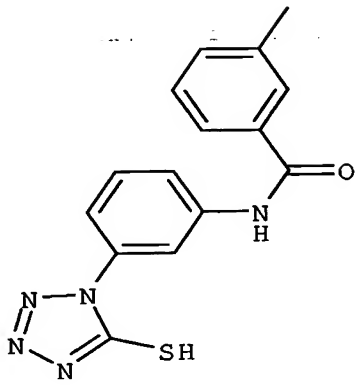


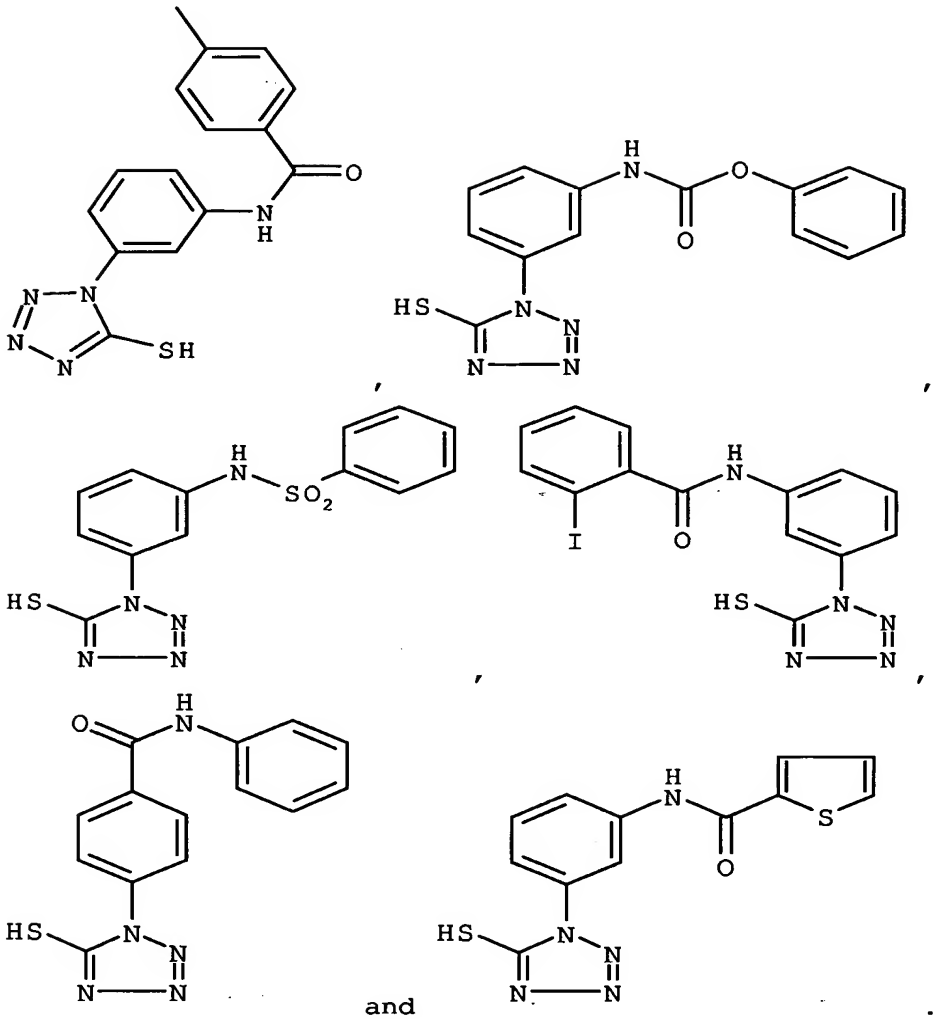






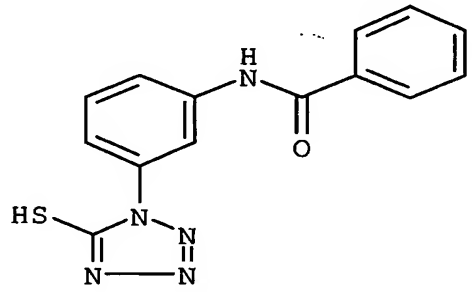


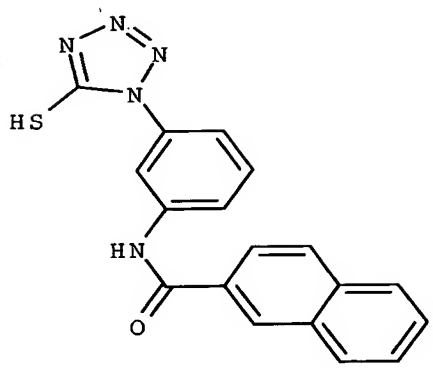
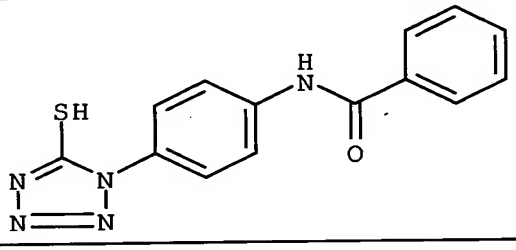
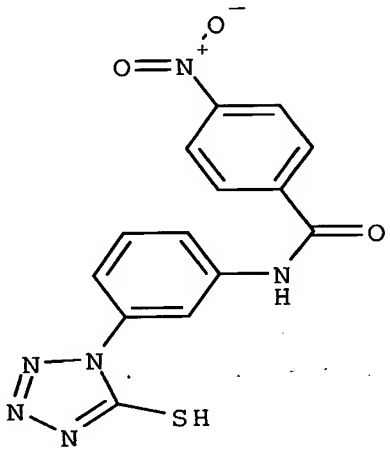
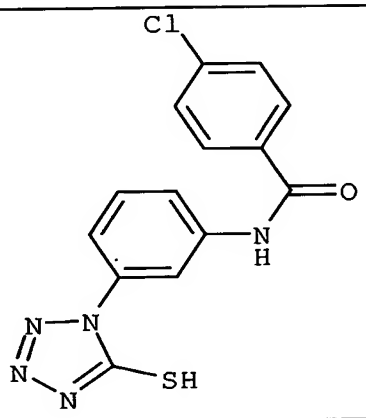


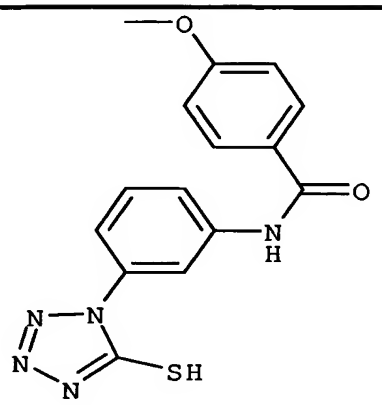
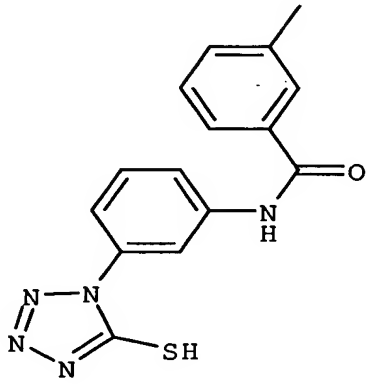
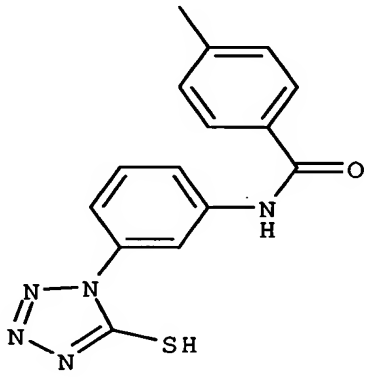
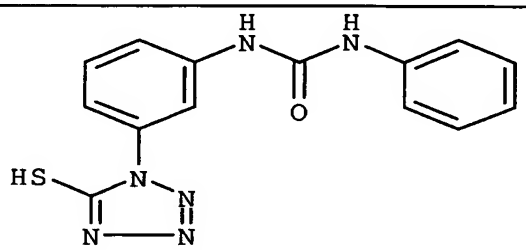
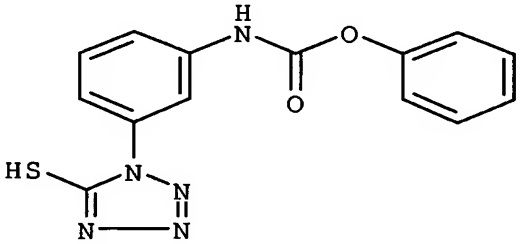


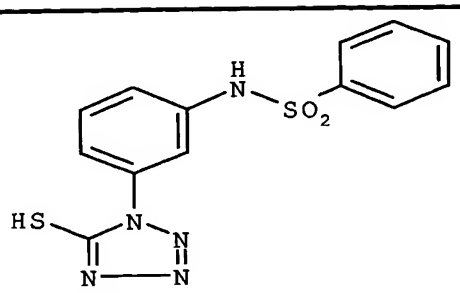
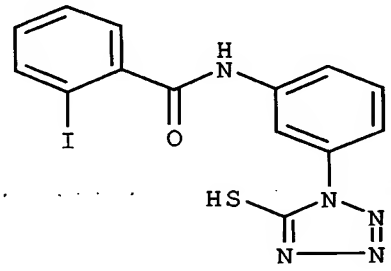
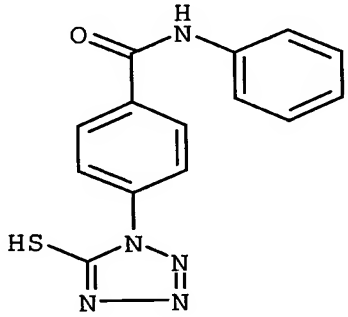
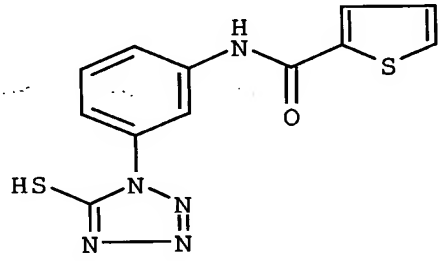
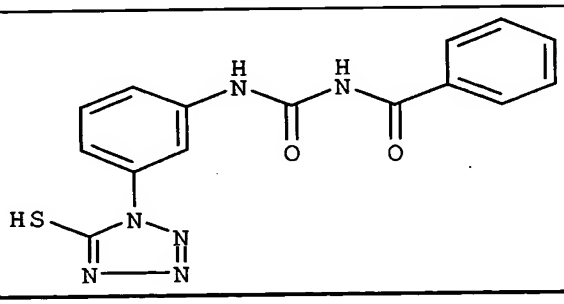
and

Suitable 1-phenyl-5-mercaptotetrazole (PMT) compounds in which the phenyl group is substituted with a substituent containing an optionally substituted aryl group, according to the present invention, include:

PMT-nr.	Structure	
PMT-1		1-(3'-benzoyl-amino-phenyl)-5-mercapto-tetrazole

PMT-2		1-[3'-(2-naphthoyl-amino)-phenyl]-5-mercapto-tetrazole
PMT-3		1-[4'-(benzoyl-amino)-phenyl]-5-mercapto-tetrazole
PMT-4		1-[3'-(p-nitro-benzoyl-amino)-phenyl]-5-mercapto-tetrazole
PMT-5		1-[3'-(p-chloro-benzoyl-amino)-phenyl]-5-mercapto-tetrazole

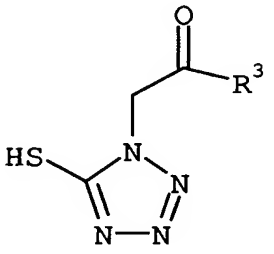
PMT-6		1-[3'-(p-methoxy-benzoyl-amino)-phenyl]-5-mercapto-tetrazole
PMT-7		1-[3'-(m-methyl-benzoyl-amino)-phenyl]-5-mercapto-tetrazole
PMT-8		1-[3'-(p-methyl-benzoyl-amino)-phenyl]-5-mercapto-tetrazole
PMT-9		
PMT-10		

PMT-11		
PMT-12		
PMT-13		
PMT-14		
PMT-15		

1-(5-mercapto-1-tetrazolyl)-acetyl compounds

The substantially light-insensitive black and white monosheet thermographic recording material of the present invention can

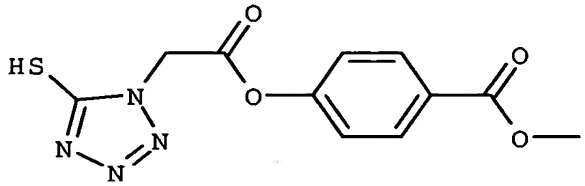
contain at least one 1-(5-mercapto-1-tetrazolyl)-acetyl compound represented by formula (III):



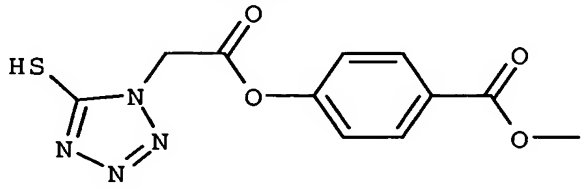
(III)

wherein R^3 is $-NR^4R^5$, $-OR^6$ or an optionally substituted aryl or heteroaryl group; R^4 is hydrogen or an optionally substituted alkyl, aryl or heteroaryl group; R^5 is an optionally substituted aryl or heteroaryl group; and R^6 is an optionally substituted aryl group.

According to a fourth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the at least one stabilizer is

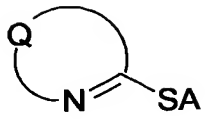


Suitable 1-(5-mercapto-1-tetrazolyl)-acetyl (MTA) compounds according to formula (III), according to the present invention, include:

	Structure
MTA-1	

Bis[mercaptoheterocyclic] compounds

The substantially light-insensitive black and white monosheet thermographic recording material of the present invention can contain at least one compound with two or more groups represented by formula (IV):

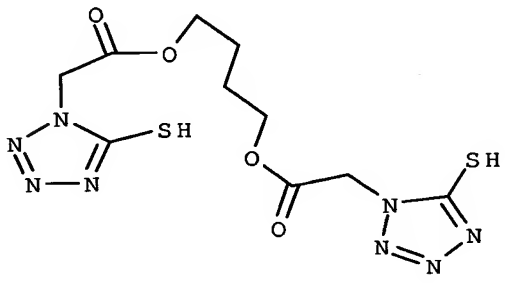


(IV)

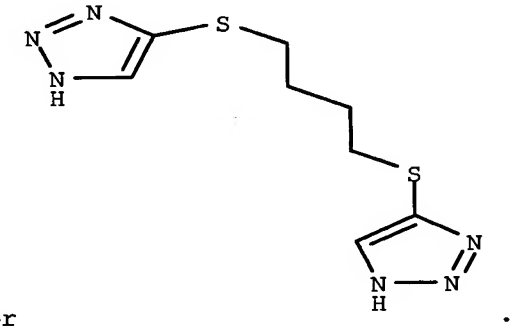
where Q comprises the necessary atoms to form a 5- or 6-membered unsaturated heterocyclic ring, A is hydrogen, a counterion to compensate the negative charge of the thiolate group or two or more A groups provide a linking group between the two or more groups represented by formula (IV).

According to a fifth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, at least one of the 5- or 6-membered unsaturated heterocyclic ring is a pyridine, a pyrazine, a pyrimidine, a triazine, a pyrrole, a 1,2,3-triazole, a 1,2,4-triazole, a tetrazole, an oxadiazole, a thiadiazole, an oxazole, an iso-oxazole, a thiazole, an iso-thiazole or an imidazole ring. Such rings may also be annelated with an aromatic ring system.

According to a sixth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the at least one stabilizer is

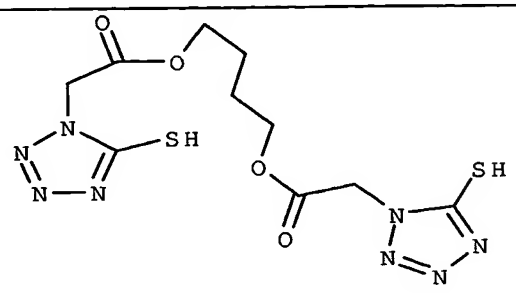


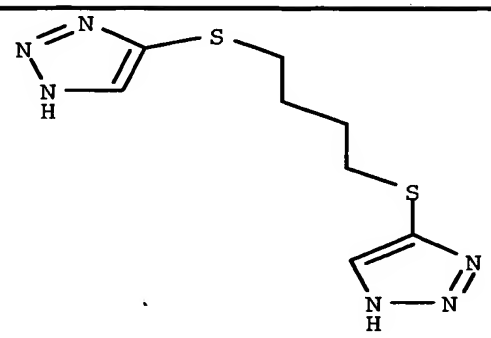
or



.

Suitable compounds represented by formula (IV), according to the present invention, include:

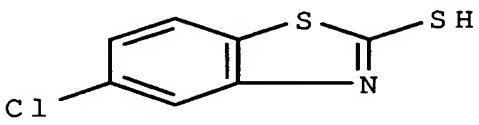
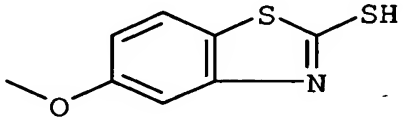
	Structure
Compound-1	

Compound-2	

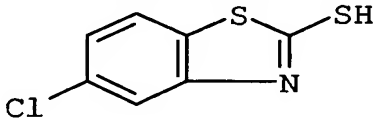
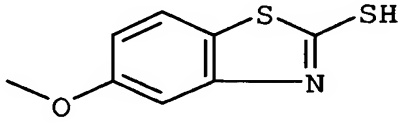
2-mercapto-benzothiazole compounds

The substantially light-insensitive black and white monosheet thermographic recording material of the present invention can contain at least one 2-mercapto-benzothiazole compound substituted by an alkyl, an aryl, an alkoxy, a nitro, a cyano or an acyl group or a halogen atom.

According to a seventh embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the at least one stabilizer is

 or 

Suitable 2-mercapto-benzothiazole (MBT), according to the present invention, include:

MBT-nr.	Structure
MBT-1	
MBT-2	

Organic silver salt

According to a fourth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material of the present invention, the organic silver salts are not

double organic salts containing a silver cation associated with a second cation e.g. magnesium or iron ions.

According to a fifth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material of the present invention, at least one of the organic silver salts is a substantially light-insensitive silver salt of an organic carboxylic acid.

According to a sixth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material of the present invention, at least one of the organic silver salts is a substantially light-insensitive silver salt of an aliphatic carboxylic acids known as a fatty acid, wherein the aliphatic carbon chain has preferably at least 12 C-atoms, e.g. silver laurate, silver palmitate, silver stearate, silver hydroxystearate, silver oleate and silver behenate, which silver salts are also called "silver soaps". Other silver salts of an organic carboxylic acid as described in GB-P 1,439,478, e.g. silver benzoate, may likewise be used to produce a thermally developable silver image. Combinations of different silver salt of an organic carboxylic acids may also be used in the present invention, as disclosed in EP-A 964 300.

Organic silver salts may be dispersed by standard dispersion techniques. Ball mills, bead mills, microfluidizers, ultrasonic apparatuses, rotor stator mixers etc. have been found to be useful in this regard. Mixtures of organic silver salt dispersions produced by different techniques may also be used to obtain the desired thermographic properties e.g. of coarser and more finely ground dispersions of organic silver salts.

Reducing agents

According to an seventh embodiment of the black and white thermographic recording material, according to the present invention, the reducing agent is an organic compound containing at least one active hydrogen atom linked to O, N or C, such as is the case with, aromatic di- and tri-hydroxy compounds. 1,2-dihydroxy-benzene derivatives, such as catechol, 3-(3,4-dihydroxyphenyl) propionic acid, 1,2-dihydroxybenzoic acid, gallic acid and esters e.g. methyl gallate, ethyl gallate, propyl gallate, tannic acid, and 3,4-dihydroxy-benzoic acid esters are preferred, with those described in EP-A 0 692 733 and EP-A 0 903 625 being particularly preferred.

Combinations of reducing agents may also be used that on heating become reactive partners in the reduction of the one or more substantially light-insensitive organic silver salt. For example, combinations of sterically hindered phenols with sulfonyl hydrazide reducing agents such as disclosed in US 5,464,738; trityl hydrazides and formyl-phenyl-hydrazides such as disclosed in US 5,496,695; trityl hydrazides and formyl-phenyl-hydrazides with diverse auxiliary reducing agents as disclosed in US 5,545,505, US 5,545,507 and US 5,558,983; acrylonitrile compounds as disclosed in US 5,545,515 and US 5,635,339; and 2-substituted malonodialdehyde compounds as disclosed in US 5,654,130.

Binder of the thermosensitive element

The film-forming binder of the thermosensitive element may be all kinds of natural, modified natural or synthetic resins or mixtures of such resins, in which the at least one organic silver salt can be dispersed homogeneously either in aqueous or solvent media: e.g. cellulose derivatives, starch ethers, galactomannan, polymers derived from α,β-ethylenically unsaturated compounds such as polyvinyl chloride, after-chlorinated polyvinyl chloride, copolymers of vinyl chloride and vinylidene chloride, copolymers of vinyl chloride and vinyl acetate, polyvinyl acetate and partially hydrolyzed polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals that are made from polyvinyl alcohol as starting material in which only a part of the repeating vinyl alcohol units may have reacted with an aldehyde, preferably polyvinyl butyral, copolymers of acrylonitrile and acrylamide, polyacrylates, polymethacrylates, polystyrene and polyethylene or mixtures thereof.

Suitable water-soluble film-forming binders for use in thermographic recording materials according to the present invention are: polyvinyl alcohol, polyacrylamide, polymethacrylamide, polyacrylic acid, polymethacrylic acid, polyvinylpyrrolidone, polyethyleneglycol, proteinaceous binders, polysaccharides and water-soluble cellulose derivatives. A preferred water-soluble binder for use in the thermographic recording materials of the present invention is gelatine.

The binder to organic silver salt weight ratio is preferably in the range of 0.2 to 7, and the thickness of the thermosensitive element is preferably in the range of 5 to 50 μm. Binders are preferred which do not contain additives, such as certain antioxidants (e.g. 2,6-di-tert-butyl-4-methylphenol), or impurities

which adversely affect the thermographic properties of the thermographic recording materials in which they are used.

Toning agent

According to an eighth embodiment of the black and white monosheet thermographic recording material, according to the present invention, the thermosensitive element contains a toning agent, which enables a neutral black image tone to be obtained in the higher densities and neutral grey in the lower densities.

According to a ninth embodiment of the black and white monosheet thermographic recording material, according to the present invention, the thermosensitive element further contains a toning agent selected from the group consisting of phthalimides, phthalazinones, benzoxazine diones and naphthoxazine diones e.g. phthalimides and phthalazinones within the scope of the general formulae described in US 4,082,901; the toning agents described in US 3,074,809, 3,446,648 and 3,844,797; and the heterocyclic toner compounds of the benzoxazine dione or naphthoxazine dione type as disclosed in GB 1,439,478, US 3,951,660 and US 5,599,647, herein incorporated by reference.

According to a tenth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the substantially light-insensitive thermographic material contains a thermosensitive element, the thermosensitive element containing one or more toning agents selected from the group consisting of phthalazinone, benzo[e][1,3]oxazine-2,4-dione, 7-methyl-benzo[e][1,3]oxazine-2,4-dione, 7-methoxy-benzo[e][1,3]oxazine-2,4-dione and 7-(ethylcarbonato)-benzo[e][1,3]oxazine-2,4-dione.

Auxiliary antifoggants

According to an eleventh embodiment of the black and white monosheet thermographic recording material, according to the present invention, the thermographic recording material further contains an auxiliary antifoggant to obtain improved shelf-life and reduced fogging.

According to a twelfth embodiment of the black and white monosheet thermographic recording material, according to the present invention, the thermographic recording material further contains an antifoggant selected from the group consisting of

benzotriazole, substituted benzotriazoles and aromatic polycarboxylic acid such as ortho-phthalic acid, 3-nitro-phthalic acid, tetrachlorophthalic acid, mellitic acid, pyromellitic acid and trimellitic acid and anhydrides thereof.

According to a thirteenth embodiment of the black and white monosheet thermographic recording material, according to the present invention, the thermosensitive element further contains an optionally substituted benzotriazole.

Polycarboxylic acids and anhydrides thereof

According to a fourteenth embodiment of the black and white monosheet thermographic recording material, according to the present invention, the thermosensitive element further contains at least one polycarboxylic acid and/or anhydride thereof in a molar percentage of at least 15 with respect to all the organic silver salt(s) present and in thermal working relationship therewith. The polycarboxylic acid may be aliphatic (saturated as well as unsaturated aliphatic and also cycloaliphatic) or an aromatic polycarboxylic acid, may be substituted and may be used in anhydride form or partially esterified on the condition that at least two free carboxylic acids remain or are available in the heat recording step.

Surfactants and dispersants

Surfactants and dispersants aid the dispersion of ingredients which are insoluble in the particular dispersion medium. The substantially light-insensitive thermographic material used in the present invention may contain one or more surfactants, which may be anionic, non-ionic or cationic surfactants and/or one or more dispersants. Suitable dispersants are natural polymeric substances, synthetic polymeric substances and finely divided powders, e.g. finely divided non-metallic inorganic powders such as silica.

Support

According to a fifteenth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the support is transparent or translucent. It is preferably a thin flexible

carrier made transparent resin film, e.g. made of a cellulose ester, e.g. cellulose triacetate, polypropylene, polycarbonate or polyester, e.g. polyethylene terephthalate. The support may be in sheet, ribbon or web form and subbed if needs be to improve the adherence to the thereon coated thermosensitive element. The support may be dyed or pigmented to provide a transparent coloured background for the image.

Protective layer

According to a fifteenth embodiment of the substantially light-insensitive black and white monosheet thermographic recording material, according to the present invention, the thermosensitive element is provided with a protective layer. In general this protects the thermosensitive element from atmospheric humidity and from surface damage by scratching etc. and prevents direct contact of printheads or heat sources with the recording layers. Protective layers for thermosensitive elements which come into contact with and have to be transported past a heat source under pressure, have to exhibit resistance to local deformation and good slipping characteristics during transport past the heat source during heating. A slipping layer, being the outermost layer, may comprise a dissolved lubricating material and/or particulate material, e.g. talc particles, optionally protruding from the outermost layer. Examples of suitable lubricating materials are a surface active agent, a liquid lubricant, a solid lubricant or mixtures thereof, with or without a polymeric binder.

Coating techniques

The coating of any layer of the substantially light-insensitive thermographic material used in the present invention may proceed by any coating technique e.g. such as described in Modern Coating and Drying Technology, edited by Edward D. Cohen and Edgar B. Gutoff, (1992) VCH Publishers Inc., 220 East 23rd Street, Suite 909 New York, NY 10010, USA. Coating may proceed from aqueous or solvent media with overcoating of dried, partially dried or undried layers.

Thermographic processing

Thermographic imaging is carried out by the image-wise application of heat either in analogue fashion by direct exposure through an image or by reflection from an image, or in digital fashion pixel by pixel either by using an infra-red heat source, for example with a Nd-YAG laser or other infra-red laser, with a substantially light-insensitive thermographic material preferably containing an infra-red absorbing compound, or by direct thermal imaging with a thermal head.

In thermal printing image signals are converted into electric pulses and then through a driver circuit selectively transferred to a thermal printhead. The thermal printhead consists of microscopic heat resistor elements, which convert the electrical energy into heat via Joule effect. The operating temperature of common thermal printheads is in the range of 300 to 400°C and the heating time per picture element (pixel) may be less than 1.0ms, the pressure contact of the thermal printhead with the recording material being e.g. 200-1000g/linear cm, i.e. with a contact zone (nip) of 200 to 300 μm a pressure of 5000 to 50,000 g/cm^2, to ensure a good transfer of heat.

In order to avoid direct contact of the thermal printing heads with the outermost layer on the same side of the support as the thermosensitive element when this outermost layer is not a protective layer, the image-wise heating of the recording material with the thermal printing heads may proceed through a contacting but removable resin sheet or web wherefrom during the heating no transfer of recording material can take place.

Activation of the heating elements can be power-modulated or pulse-length modulated at constant power. EP-A 654 355 discloses a method for making an image by image-wise heating by means of a thermal head having energizable heating elements, wherein the activation of the heating elements is executed duty cycled pulsewise. EP-A 622 217 discloses a method for making an image using a direct thermal imaging element producing improvements in continuous tone reproduction.

Image-wise heating of the recording material can also be carried out using an electrically resistive ribbon incorporated into the material. Image- or pattern-wise heating of the recording material may also proceed by means of pixel-wise modulated ultra-sound.

Industrial application

Thermographic imaging can be used for the production of reflection type prints and transparencies, in particular for use in the medical diagnostic field in which black-imaged transparencies are widely used in inspection techniques operating with a light box.

The invention is illustrated hereinafter by way of comparative examples and invention examples. The percentages and ratios given in these examples are by weight unless otherwise indicated.

Subbing layers on the emulsion side of the support:

Subbing layer Nr. 01 has the composition:

copolymer of 88% vinylidene chloride, 10% methyl acrylate and 2% itaconic acid	79.1 mg/m^2
Kieselsol® 100F, a colloidal silica from BAYER	18.6 mg/m^2
Mersolat® H, a surfactant from BAYER	0.4 mg/m^2
Ultravon® W, a surfactant from CIBA-GEIGY	1.9 mg/m^2

Subbing layer Nr. 02 has the composition:

copolymer of 88% vinylidene chloride, 10% methyl acrylate and 2% itaconic acid	151 mg/m^2
Kieselsol® 100F, a colloidal silica from BAYER	35 mg/m^2
Mersolat® H, a surfactant from BAYER	0.75 mg/m^2

Ingredients in the thermosensitive element in addition to the above-mentioned ingredients:

BL5HP = S-LEC BL5HP, a polyvinyl butyral from SEKISUI;
Oil = BAYSILON, a silicone oil from BAYER;
VL = DESMODUR VL, a 4,4'-diisocyanatodiphenylmethane from BAYER;

Reducing agents:
R01 = 3,4-dihydroxybenzonitrile;
R02 = 3,4-dihydroxybenzophenone;

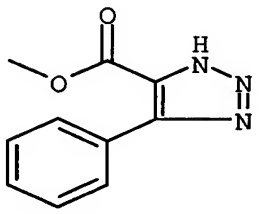
Toning agent:
T01 = 7-(ethylcarbonato)-benzo[e][1,3]oxazine-2,4-dione;
T02 = 7-methyl-benzo[e][1,3]oxazine-2,4-dione;

Stabilizers:
S01 = glutaric acid

S02 = tetrachlorophthalic acid anhydride

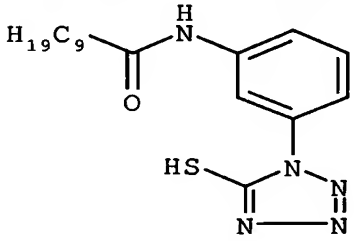
S03 = benzotriazole

S04 =

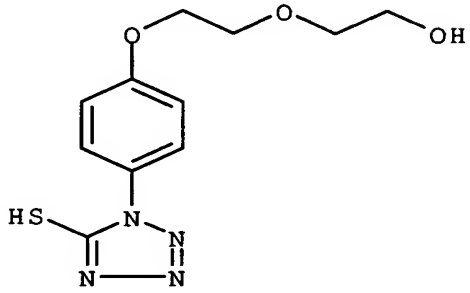


PMT-C1 = 1-phenyl-5-mercapto-tetrazole

PMT-C2 =



PMT-C3 =



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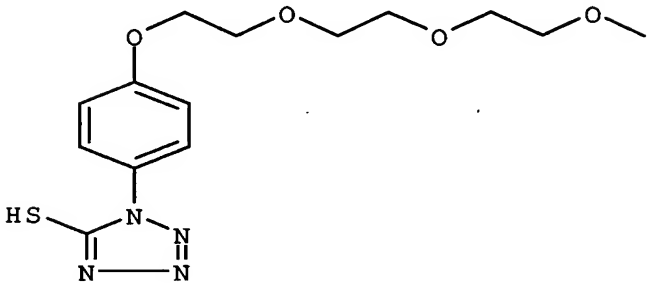
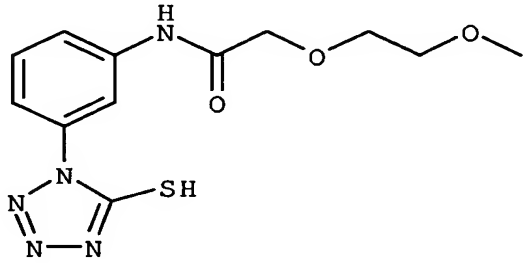
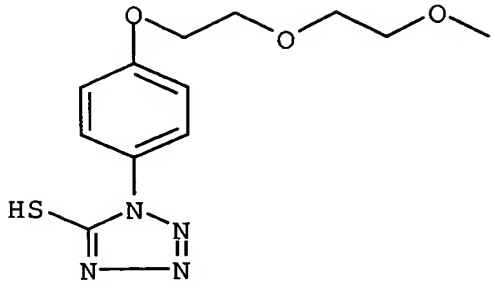


PMT-C5 =



PMT-C6 =



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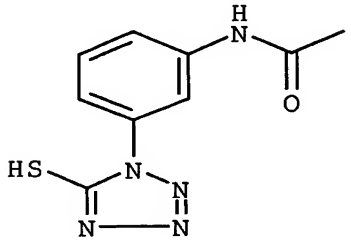

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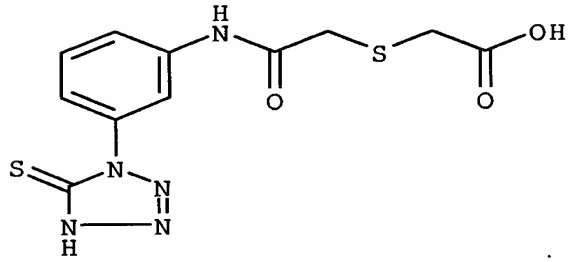

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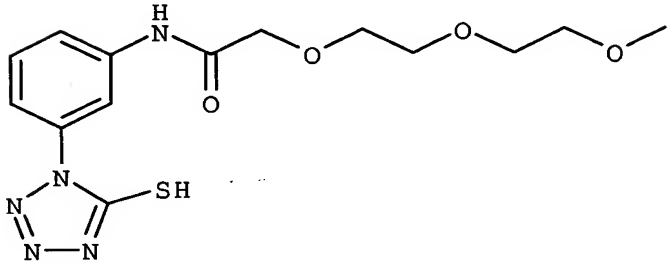

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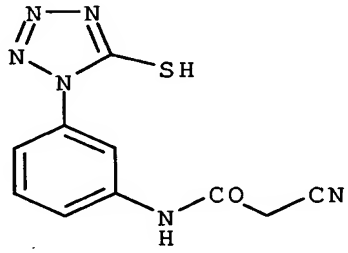

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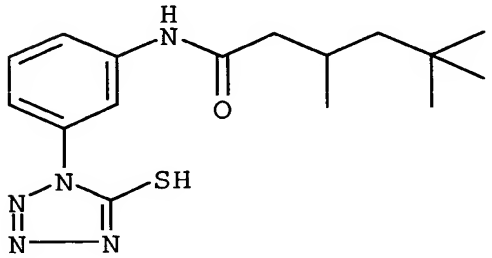
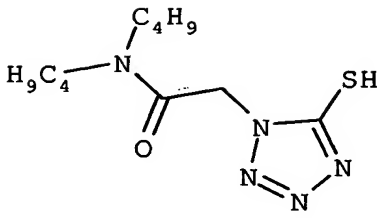


MTA-C1 =



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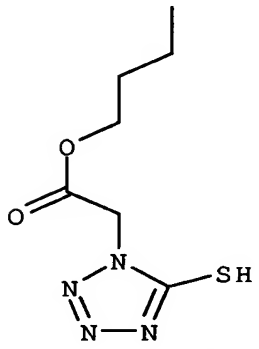

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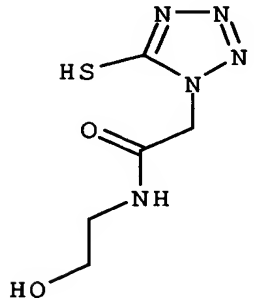

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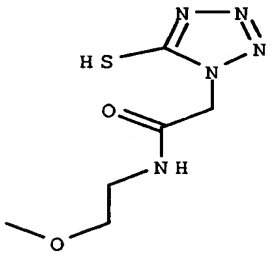

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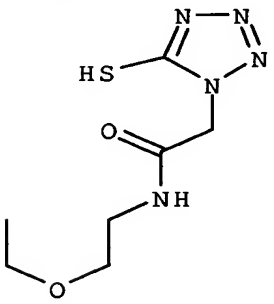
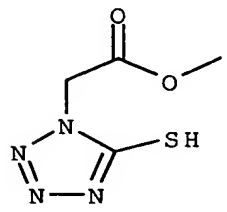


MTA-C6 =



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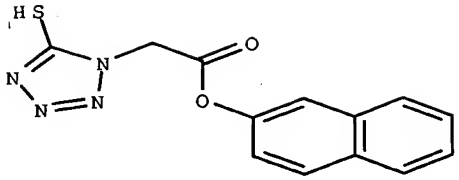
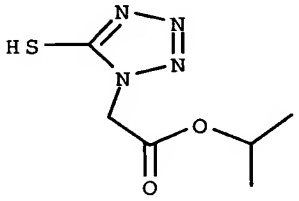


MTA-C8 =



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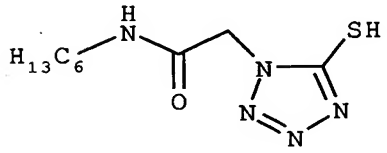

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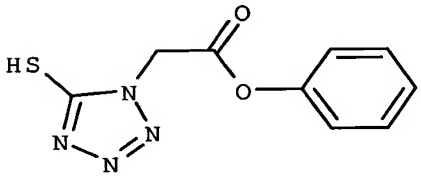
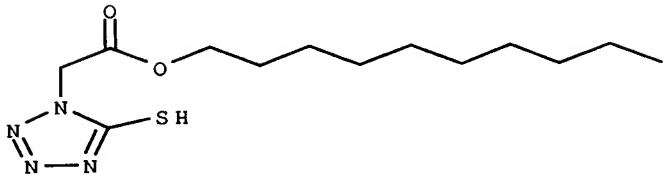
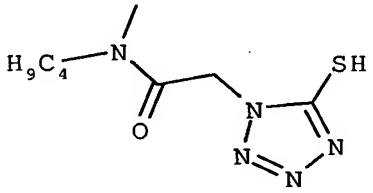


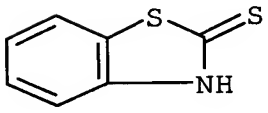
MTA-C11 =



MTA-C12 =

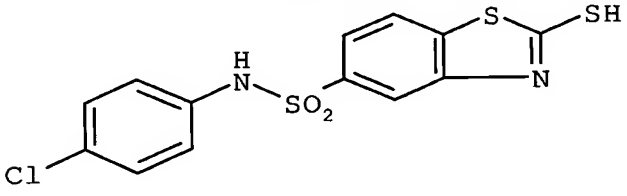


MBT-C1 =



2-mercapto-benzothiazole

MBT-C2 =



Ingredients in the protective layer:

ERCOL™ 48 20 = a polyvinylalcohol from ACETEX EUROPE;

LEVASIL™ VP AC 4055 = a 15% aqueous dispersion of colloidal silica with acid groups predominantly

		neutralized with sodium ions and a specific surface are of 500 m^2/g, from BAYER AG has been converted into the ammonium salt;
ULTRAVON™ W	=	75-85% concentrate of a sodium arylsulfonate from Ciba Geigy converted into acid form by passing through an ion exchange column;
SYLOID™ 72	=	a silica from Grace;
SERVOXYL™ VPDZ 3/100	=	a mono[isotridecyl polyglycolether (3 EO)] phosphate, from SERVO DELDEN B.V.;
SERVOXYL™ VPAZ 100	=	a mixture of monolauryl and dilauryl phosphate, from SERVO DELDEN B.V.;
MICROACE TALC P3	=	an Indian talc from NIPPON TALC;
RILANIT™ GMS	=	a glycerine monotallow acid ester, from HENKEL AG
TMOS	=	tetramethylorthosilicate hydrolyzed in the presence of methanesulfonic acid.

COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2

The substantially light-insensitive thermographic materials of COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 were prepared by coating a dispersion with the following ingredients in 2-butanone onto a 175µm thick blue-pigmented polyethylene terephthalate support with CIELAB a*- and b*- values of -9.5 and -17.9 respectively subbed on the emulsion-coated side with subbing layer 01 giving layers after drying at 50°C for 1h in a drying cupboard with the compositions given in Table 1.

Table 1:

Comparative example nr.	stabilizer type	stabilizer conc. mol% vs AgB	AgBeh coverage [g/m^2]	BL5HP [g/m^2]	R01 mol% vs AgB	R02 mol% vs AgB	T01 mol% vs AgB	T02 mol% vs AgB	S01 mol% vs AgB	S02 mol% vs AgB	VL [g/m^2]	Oil [g/m^2]
1	S03	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035
2	PMT-C1	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035
3	PMT-C2	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035
4	MTA-C1	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035
5	MTA-C2	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035
6	MBT-C1	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035
Invention example nr												
1	MBT-1	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035
2	MBT-2	10	3.89	15.12	50	30	5	10	22	5	0.17	0.035

The thermosensitive elements were then coated with an aqueous composition with the following ingredients, which was adjusted to a pH of 3.8 with 1N nitric acid, to a wet layer thickness of 85 µm and then dried at 50°C for 15 minutes to produce a protective layer PRO-L with the composition:

ERCOL™ 48 20	=	2.1g/m^2
LEVASIL™ VP AC 4055	=	1.05g/m^2
ULTRAVON™ W	=	0.075g/m^2
SYLOID™ 72	=	0.09 g/m^2
SERVOXYL™ VPDZ 3/100	=	0.075g/m^2
SERVOXYL™ VPAZ 100	=	0.075g/m^2
MICROACE TALC P3	=	0.045g/m^2
RILANIT™ GMS	=	0.15g/m^2
TMOS	=	0.87g/m^2 (assuming that the TMOS was completely converted to SiO_2)

After coating the protective layer was hardened by heating the substantially light-insensitive thermographic material at 45°C for 7 days at a relative humidity of 70%.

Thermographic printing

The substantially light-insensitive thermographic recording materials of COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 were printed using a DRYSTAR™ 4500 printer from AGFA-GEVAERT

with a resolution of 508 dpi which had been modified to operate at a printing speed of 14 mm/s and a line-time of 3.5 ms instead of 7.1 ms and in which the 75 µm long (in the transport direction) and 50 µm wide thermal head resistors were power-modulated to produce different image densities.

The maximum densities of the images (D_{max}) measured through a visible filter with a MACBETH™ TR924 densitometer were all greater than 2.2.

Evaluation of thermographic properties

The image tone of fresh prints made with the substantially light-insensitive thermographic recording materials of COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 was assessed on the basis of the L*, a* and b* CIELAB-values at optical densities, D, of 1.0 and 2.0 and the results given in Table 2.

Archivability tests:

Simulated long-term archivability tests were performed by heating prints made with the substantially light-insensitive thermographic recording materials of COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 at 57°C in 34% relative humidity in the dark for 3 days and determining the shifts in CIELAB a*- and b*-values. The results are also given in Table 2.

Light-box tests:

Light-box tests were performed by exposing the substantially light-insensitive thermographic materials of COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 for 3 days on top of the white PVC window of a specially constructed light-box placed in a Votsch conditioning cupboard set at 30°C and a relative humidity of 85%. Only a central area of the window 550mm long by 500mm wide was used for mounting the test materials to ensure uniform exposure.

The stainless steel light-box used was 650mm long, 600mm wide and 120mm high with an opening 610mm long and 560mm wide with a rim 10mm wide and 5mm deep round the opening, thereby forming a platform for a 5mm thick plate of white PVC 630mm long and 580mm wide, making the white PVC-plate flush with the top of the light-box and preventing light loss from the light-box other than through the white PVC-plate. This light-box was fitted with 9 Planilux? TLD

36W/54 fluorescent lamps 27mm in diameter mounted length-wise equidistantly from the two sides, with the lamps positioned equidistantly to one another and the sides over the whole width of the light-box and with the tops of the fluorescent tubes 30mm below the bottom of the white PVC plate and 35mm below the materials being tested. The shifts in CIELAB a*- and b*-values at an optical density, D, of 1.0 and the shift in the CIELAB b*-value were determined for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 and the results are also given in Table 2.

In light-box tests the substantially light-insensitive thermographic recording materials of INVENTION EXAMPLES 1 and 2 containing the compounds MBT-1 and MBT-2 respectively, according to the present invention, exhibit substantially lower shifts in CIELAB a*- and b*-values at an optical density, D, of 1.0 and in CIELAB b*-value at Dmin than that of COMPARATIVE EXAMPLE 6 containing the compound MBT-C1. Thus the substituted 2-mercapto-benzothiazoles MBT-1 and MBT-2 endow substantially light-insensitive thermographic recording materials with a substantially higher light stability than unsubstituted 2-mercapto-benzothiazole, MBT-C1.

Table 2:

Comparative Example nr.	stabilizer type	CIELAB-values of prints with fresh film				Shift in CIELAB-values of prints after 3d/57°C/ 34%RH in dark		Shift of CIELAB-values of prints after 3d/30°C/85%RH light-box exposure		
		D = 1.0		D = 2.0		D = 1.0		D = 1.0		Dmin
		a*	b*	a*	b*	Δa*	Δb*	Δa*	Δb*	Δb*
1	S03	-3.48	-5.92	-1.24	-4.77	+0.02	-0.81	-0.52	+2.57	+5.15
2	PMT-C1	-3.65	-4.23	-1.82	-3.64	-0.44	-0.82	-0.51	+2.80	**+6.46**
3	PMT-C2	-1.31	-5.59	**+4.96**	**+1.56**	-0.12	+0.57	-0.44	0	**+3.12**
4	MTA-C1	-2.59	-4.57	**+2.21**	-1.09	+1.36	+0.36	-0.32	+1.27	**+4.04**
5	MTA-C2	-3.66	-5.17	-1.47	-3.72	-0.26	-0.79	-0.48	+4.54	**+10.6**
6	MBT-C1	-4.15	-4.71	-2.11	-3.75	+0.25	+0.86	+1.45	**+12.04**	**+16.53**
Invention Example										
1	MBT-1	-4.49	-7.59	-2.7	-5.13	+0.26	+0.35	+0.29	+5.61	+6.14
2	MBT-2	-4.69	-6.06	-2.54	-3.74	+0.63	+0.77	-0.07	+3.5	+4.55

COMPARATIVE EXAMPLES 7 to 18 and INVENTION EXAMPLES 3 to 18

The substantially light-insensitive thermographic materials of COMPARATIVE EXAMPLES 7 to 18 and INVENTION EXAMPLES 3 to 18 were prepared by coating a dispersion with the following ingredients in 2-butanone onto the support described for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 giving layers after drying at 85°C for 3 minutes in a drying cupboard with the compositions given in Table 3.

Table 3:

Comparative example nr.	stabilizer of present invention		AgBeh coverage [g/m^2]	BL5HP [g/m^2]	R01 mol% vs AgB	R02 mol% vs AgB	T02 mol% vs AgB	S01 mol% vs AgB	S02 mol% vs AgB	VL [g/m^2]	Oil [g/m^2]
	type	mol% vs AgB									
7	S03	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
8	PMT-C2	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
9	PMT-C3	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
10	PMT-C4	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
11	PMT-C5	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
12	PMT-C6	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
13	MTA-C3	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
14	MTA-C4	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
15	MTA-C5	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
16	MTA-C12	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
17	MBT-C2	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
Invention example nr											
3	PMT-1	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
4	PMT-2	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
5	PMT-3	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
6	PMT-4	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
7	PMT-5	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
8	PMT-6	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
9	PMT-7	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
10	PMT-8	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
11	PMT-9	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
12	PMT-10	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
13	PMT-11	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
14	PMT-12	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
15	PMT-13	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
16	MTA-1	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
17	S04	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037
18	Compound 2	10	4.15	16.6	35	45	15	24	4.91	0.19	0.037

The thermosensitive elements were then provided with a protective layer as described for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2.

The thermographic properties of the substantially light-insensitive thermographic recording materials of COMPARATIVE EXAMPLES 7 to 18 and INVENTION EXAMPLES 3 to 18 were evaluated as described for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2 except that the light-box tests for COMPARATIVE EXAMPLES 8, 14, 15, 16 and 17 and INVENTION EXAMPLES 13 to 16, as indicated in Table 4, were carried out using a PLANILUX™ light-box DX 105x43 cm/EHR-AP with a maximum light intensity of ca. 4700 cd/m^2 having a length of 1235 cm, width of 62 cm and depth of 10 cm, a surface of 105 cm x 42 cm being used, and were exposed for 2 days under ambient conditions. The results are given in Table 4.

Table 4:

Comparative Example nr.	stabilizer type	CIELAB-values of prints with fresh film				Shift in CIELAB-values of prints after 3d/57°C/ 34%RH in dark		Shift of CIELAB-values of prints after 3d/30°C/85%RH light-box exposure		
		D = 1.0		D = 2.0		D = 1.0		D = 1.0		Dmin
		a*	b*	a*	b*	Δa*	Δb*	Δa*	Δb*	Δb*
7	S03	-2.18	-9.19	+0.74	-6.64	-0.51	+2.71	0.0	+0.98	**+2.73**
8#	S03	-2.24	-8.82	+0.70	-6.59	-0.72	+1.95	-0.03	+0.26	+1.67
9	PMT-C2	+1.23	-6.78	**+7.81**	**+3.0**	-1.35	**+10.8**	-0.15	+0.14	+1.06
10	PMT-C3	-2.41	-6.51	-0.31	-4.47	+0.44	**+5.77**	+0.47	**+5.58**	**+9.7**
11	PMT-C4	+0.61	-2.49	**+6.42**	**+1.64**	+2.18	**+14.31**	+0.96	**+7.23**	**+2.81**
12	PMT-C5	-3.32	-6.14	-0.81	-2.91	-0.06	**+4.48**	-0.25	**+9.84**	**+9.02**
13	PMT-C6	-1.20	-4.56	**+3.22**	**+0.75**	+0.22	**+10.73**	-0.48	**+6.99**	**+3.11**
14#	MTA-C3	-2.59	-7.41	-0.01	-4.36	-0.6	+0.33	-0.8	**+8.15**	**+11.11**
15#	MTA-C4	-3.26	-5.54	-0.28	**-0.93**	-0.54	+0.18	-0.58	**+9.8**	**+16.56**
16#	MTA-C5	-2.70	-4.85	**+1.65**	**+0.30**	-0.40	+0.11	-0.23	**+10.93**	**+20.42**
17#	MTA-C12	-1.65	-8.07	**+3.60**	-3.63	-0.65	+3.82	-0.35	+0.32	+1.06
18	MBT-C2	-2.04	-9.88	+0.80	-7.27	+0.21	**+8.72**	+0.1	+0.17	+1.12
Invention Example										

3	PMT-1	-2.78	-7.59	+0.25	-5.54	-0.08	+5.58	-0.51	+0.86	+2.17
4	PMT-2	-3.14	-6.89	-0.67	-5.55	-0.69	+2.56	-0.23	+0.45	+0.81
5	PMT-3	-2.34	-8.15	+0.41	-6.29	-0.74	+3.95	+0.05	+1.17	+1.37
6	PMT-4	-2.60	-7.32	-0.35	-6.18	-1.04	+2.47	-0.05	-0.02	+0.88
7	PMT-5	-2.49	-8.25	+0.77	-5.58	-1.3	+2.26	-0.19	+0.49	+1.11
8	PMT-6	-3.49	-7.31	-1.03	-6.12	-0.45	+2.71	-0.01	-0.24	+1.17
9	PMT-7	-3.37	-6.94	-0.65	-5.58	-0.38	+1.77	-0.01	-0.44	+0.71
10	PMT-8	-3.25	-7.87	+0.05	-5.50	-0.29	+2.62	0	+0.27	+1.89
11	PMT-9	-1.40	-8.50	+3.99	-4.27	-0.94	+1.49	-0.38	+0.2	+2.05
12	PMT-10	-2.87	-6.93	+0.17	-5.09	-0.9	+0.74	-0.02	+0.31	+2.0
13#	PMT-11	-2.99	-7.58	-0.52	-5.92	-0.72	+1.31	-0.10	+0.01	+1.59
14#	PMT-12	-3.14	-6.70	-0.47	-5.12	-0.79	+1.09	+0.05	+0.51	+2.0
15#	PMT-13	-2.82	-9.13	+0.02	-6.66	-0.79	+0.66	-0.03	+1.01	+2.27
16#	MTA-1	-2.77	-8.48	-0.47	-6.34	-1.24	+1.72	-0.23	+1.58	+1.88
17	S04	-2.74	-8.01	+0.48	-5.26	-0.16	+3.27	-0.88	+2.62	+3.28
18	Comp. 2	-1.53	-8.14	+0.60	-3.66	-0.08	+3.46	-0.34	+1.6	+2.13

light-box exposure carried out for 2 days under ambient conditions in PLANILUX™ light-box DX

The results reported in Table 4 were generated with substantially light-insensitive thermographic recording materials with a different compositions from the substantially light-insensitive thermographic recording material on which the results reported in Table 2 were based, However, by comparing the results in the two table generated with substantially light-insensitive thermographic recording materials with the same stabilizer, the influence of this difference in composition can be estimated. The results for the substantially light-insensitive thermographic recording materials of COMPARATIVE EXAMPLE 1, COMPARATIVE EXAMPLE 7 and COMPARATIVE EXAMPLE 8 using stabilizer S03, benzotriazole, and those for the substantially light-insensitive thermographic recording materials of COMPARATIVE EXAMPLE 3 and COMPARATIVE EXAMPLE 9 using stabilizer PMT-C2 are given in Table 5.

Table 5:

Comparative Example nr.	stabilizer type	CIELAB-values of prints with fresh film				Shift in CIELAB-values of prints after 3d/57°C/ 34%RH in dark		Shift of CIELAB-values of prints after 3d/30°C/85%RH light-box exposure		
		D = 1.0		D = 2.0		D = 1.0		D = 1.0		Dmin
		a*	b*	a*	b*	Δa*	Δb*	Δa*	Δb*	Δb*
1	S03	-3.48	-5.92	-1.24	-4.77	+0.02	-0.81	-0.52	+2.57	+5.15
7	S03	-2.18	-9.19	+0.74	-6.64	-0.51	+2.71	0.0	+0.98	**+2.73**
8	S03	-2.24	-8.82	+0.70	-6.59	-0.72	+1.95	-0.03#	+0.26#	+1.67#
3	PMT-C2	-1.31	-5.59	**+4.96**	**+1.56**	-0.12	+0.57	-0.44	0	**+3.12**
9	PMT-C2	+1.23	-6.78	**+7.81**	**+3.0**	-1.35	**+10.8**	-0.15	+0.14	+1.06

2d/ambient conditions instead of 3d/30°C/85%RH

This comparison shows that the alternative light-box test used for COMPARATIVE EXAMPLES 8, 14, 15, 16 and 17 and INVENTION EXAMPLES 13 to 16 gave comparable shifts in CIELAB a*- and b*-values to those obtained with the standard light-box test in the case of substantially light-insensitive thermographic recording materials containing 10 mol% of S03 (benzotriazole) and that the composition of substantially light-insensitive thermographic recording material used for COMPARATIVE EXAMPLES 7 to 18 and INVENTION EXAMPLES 3 to 18 gives:

- more positive a*-values at D = 1.0 and 2.0;
- more negative b*-values at D = 1.0;
- higher shifts in CIELAB values after 3d/57°C/34%RH in the dark; and
- ca. 2.0 lower shifts in CIELAB b*-values after light-box exposure;

compared with the composition of substantially light-insensitive thermographic recording materials used for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2. Bearing this information in mind the results reported in Tables 2 and 4 can be considered as a whole.

In the CIELAB-system a negative CIELAB a*-value indicates a greenish image-tone becoming greener as a* becomes more negative, a positive a*-value indicating a reddish image-tone becoming redder as a* becomes more positive. A negative CIELAB b*-value indicates a bluish tone which becomes increasingly bluer as b* becomes more negative and a positive b*-value indicates a yellowish image-tone becoming more yellow as b* becomes more positive. In terms of the visual perception of an image as a whole, the image tone of

elements of the image with a density of 1.0 have a stronger effect than the image tone of elements with lower or higher optical density.

In evaluating image tone the image tone of the SCOPIX™ LT2B silver halide emulsion laser medical hardcopy film from AGFA-GEVAERT has been used as a benchmark:

D = 1.0		D = 2.0	
CIELAB a*-value	CIELAB b*-value	CIELAB a*-value	CIELAB b*-value
-4.40	-7.5	-2.39	-3.30

Effect of 1-phenyl-5-mercapto-tetrazoles (PMT's) upon the performance of substantially light-insensitive thermographic recording materials:

If the results for substantially light-insensitive thermographic recording materials containing 1-phenyl-5-mercapto-tetrazoles (PMT's) reported in Tables 2 and 4 are considered as a whole, the following conclusions can be drawn:

- the substantially light-insensitive thermographic recording materials containing PMT-C2 exhibited prohibitively positive CIELAB a*-values, although exhibiting acceptable stability to light in the light-box test;
- the substantially light-insensitive thermographic recording materials containing PMT-C1 and PMT-C3 to PMT-C6 all exhibited poor stability to light in the light-box test as shown by high shifts in CIELAB b*-values at D = 1.0 and Dmin; and
- the substantially light-insensitive thermographic recording materials containing PMT-1 to PMT-13 all exhibited acceptable image tone and acceptable stability to light.

Effect of 2-mercapto-benzothiazoles (MBT's) upon the performance of substantially light-insensitive thermographic recording materials:

If the results for substantially light-insensitive thermographic recording materials containing 2-mercapto-benzothiazoles (MBT's) reported in Tables 2 and 4 are considered as a whole, the following conclusions can be drawn:

- the substantially light-insensitive thermographic recording material of COMPARATIVE EXAMPLE 6 containing MBT-C1 exhibited poor stability to light in the light-box test as shown by high shifts in CIELAB b*-values at D = 1.0 and Dmin;

- the substantially light-insensitive thermographic recording material of COMPARATIVE EXAMPLE 18 containing MBT-C2 exhibited poor archival stability in the archivability box test as shown by high shifts in CIELAB b*-values at D = 1.0; and
- the substantially light-insensitive thermographic recording materials of INVENTION EXAMPLES 1 and 2 containing MBT-1 and MBT-2 exhibited acceptable image tone, acceptable archival stability and much improved stability to light compared to the substantially light-insensitive thermographic recording material of COMPARATIVE EXAMPLE 6 containing MBT-C1.

Effect of 1-(5-mercapto-1-tetrazolyl)-acetyl compounds (MTA's) upon the performance of substantially light-insensitive thermographic recording materials:

If the results for substantially light-insensitive thermographic recording materials containing 1-(5-mercapto-1-tetrazolyl)-acetyl compounds (MTA's) reported in Tables 2 and 4 are considered as a whole, the following conclusions can be drawn:

- the substantially light-insensitive thermographic recording material of COMPARATIVE EXAMPLES 4 and 17 containing MTA-C1 and MTA-C12 respectively exhibited a prohibitively positive a* values of +2.21 and +3.60 respectively; and
- the substantially light-insensitive thermographic recording materials of COMPARATIVE EXAMPLE 5 and COMPARATIVE EXAMPLES 14 to 16 containing MTA-C2 and MTA-C3 to MTA-C5 respectively exhibited poor stability to light in the light-box test as shown by high shifts in CIELAB b*-values at D = 1.0 and Dmin.

INVENTION EXAMPLES 19 and 20

The substantially light-insensitive thermographic materials of INVENTION EXAMPLES 19 and 20 in which S03, benzotriazole, was used in the thermosensitive element in combination with various 1-phenyl-5-mercapto-tetrazole stabilizers were prepared by coating a dispersion with the following ingredients in 2-butanone onto a 175µm thick blue-pigmented polyethylene terephthalate support with CIELAB a*- and b*- values of -9.5 and -17.9 respectively subbed on the emulsion-coated side with subbing layer 02 giving layers after drying at 50°C for 1h in a drying cupboard with the compositions given in Table 6.

Table 6:

Invention example nr.	invention stabilizer type	invention stabilizer mol% vs AgB	AgBeh coverage [g/m^2]	BL5HP [g/m^2]	R01 mol% vs AgB	R02 mol% vs AgB	T02 mol% vs AgB	S01 mol% vs AgB	S02 mol% vs AgB	S03 mol% vs AgB	VL [g/m^2]	Oil [g/m^2]
19	PMT-1	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033
20	PMT-14	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033

The thermosensitive elements were then provided with a protective layer as described for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2.

The thermographic properties of the substantially light-insensitive thermographic recording materials of INVENTION EXAMPLES 19 and 20 were evaluated as described above for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2. The results are given in Table 7.

The results of Table 7 show that the 1-phenyl-5-mercapto-tetrazole compounds, according to the present invention, upon incorporation into the thermosensitive elements of substantially light-insensitive thermographic recording materials also provide acceptable image tone in fresh materials and acceptable stability in light-box tests when used in combination with S03, benzotriazole.

Table 7:

Invention Example nr.	stabilizer type	CIELAB-values of prints with fresh film				Shift in CIELAB-values of prints after 3d/57°C/34%RH in dark		Shift of CIELAB-values of prints after 3d/30°C/85%RH light-box exposure		
		D = 1.0		D = 2.0		D = 1.0		D = 1.0		Dmin
		a*	b*	a*	b*	Δa*	Δb*	Δa*	Δb*	Δb*
19	PMT-1	-3.0	-7.8	-0.4	-5.7	+0.3	+5.2	-0.3	+0.8	+2.4
20	PMT-14	-3.2	-6.9	-0.8	-5.3	+0.3	+4.0	-0.4	+0.7	+2.9

INVENTION EXAMPLES 21 to 25

The substantially light-insensitive thermographic materials of INVENTION EXAMPLES 21 to 25 in which S03, benzotriazole, was used in the thermosensitive element in combination with various 1-phenyl-5-mercapto-tetrazole stabilizers were prepared by coating a dispersion with the following ingredients in 2-butanone onto a 175µm thick blue-pigmented polyethylene terephthalate support with

CIELAB a*- and b*- values of -9.5 and -17.9 respectively subbed on the emulsion-coated side with subbing layer 02 giving layers after drying at 50°C for 1h in a drying cupboard with the compositions given in Table 8.

Table 8:

Invention example nr.	invention stabilizer type	invention stabilizer mol% vs AgB	AgBeh coverage [g/m^2]	BL5HP [g/m^2]	R01 mol% vs AgB	R02 mol% vs AgB	T02 mol% vs AgB	S01 mol% vs AgB	S02 mol% vs AgB	S03 mol% vs AgB	VL [g/m^2]	Oil [g/m^2]
21	PMT-1	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033
22	PMT-9	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033
23	PMT-10	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033
24	PMT-11	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033
25	PMT-12	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033

The thermosensitive elements were then provided with a protective layer as described for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2.

The thermographic properties of the substantially light-insensitive thermographic recording materials of INVENTION EXAMPLES 21 to 25 were evaluated as described above for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2. The results are given in Table 9.

Table 9:

Invention Example nr.	stabilizer type	CIELAB-values of prints with fresh film				Shift in CIELAB-values of prints after 3d/57°C/34%RH in dark		Shift of CIELAB-values of prints after 3d/30°C/85%RH light-box exposure		
		D = 1.0		D = 2.0		D = 1.0		D = 1.0		Dmin
		a*	b*	a*	b*	Δa*	Δb*	Δa*	Δb*	Δb*
21	PMT-1	-3.2	-8.9	-0.5	-6.3	+0.2	+6.8	-0.4	+2.9	+2.2
22	PMT-9	-3.1	-8.0	-0.7	-6.1	+0.2	+5.1	-0.4	+2.5	+2.7
23	PMT-10	-2.9	-9.1	+0.3	-6.2	+0.3	+6.6	-0.6	+2.1	+2.4
24	PMT-11	-3.3	-9.1	-0.7	-6.7	+0.4	+5.7	-0.4	+2.2	+2.2
25	PMT-12	-3.3	-8.5	-0.9	-6.3	+0.2	+5.7	-0.3	+2.0	+3.0

The results of Table 9 show that the 1-phenyl-5-mercapto-tetrazole compounds, according to the present invention, upon incorporation into the thermosensitive elements of substantially light-insensitive thermographic recording materials also provide

acceptable image tone in fresh materials and acceptable stability in light-box tests when used in combination with S03, benzotriazole.

INVENTION EXAMPLES 26 and 27

The substantially light-insensitive thermographic materials of INVENTION EXAMPLES 26 and 27 in which S03, benzotriazole, was used in the thermosensitive element in combination with various 1-(5-mercapto-tetrazolyl)-acetyl stabilizers were prepared by coating a dispersion with the following ingredients in 2-butanone onto a 175µm thick blue-pigmented polyethylene terephthalate support with CIELAB a*- and b*- values of -9.5 and -17.9 respectively subbed on the emulsion-coated side with subbing layer 02 giving layers after drying at 50°C for 1h in a drying cupboard with the compositions given in Table 10. The thermosensitive elements were then provided with a protective layer as described for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2.

Table 10:

Invention example nr.	invention stabilizer type	invention stabilizer mol% vs AgB	AgBeh coverage [g/m^2]	BL5HP [g/m^2]	R01 mol% vs AgB	R02 mol% vs AgB	T02 mol% vs AgB	S01 mol% vs AgB	S02 mol% vs AgB	S03 mol% vs AgB	VL [g/m^2]	Oil [g/m^2]
26	MTA-1	3	3.94	15.52	35	45	15	27	5	3	0.175	0.033
27	Compound 1	1.5	3.94	15.52	35	45	15	27	5	3	0.175	0.033

The thermographic properties of the substantially light-insensitive thermographic recording materials of INVENTION EXAMPLES 26 and 27 were evaluated as described above for COMPARATIVE EXAMPLES 1 to 6 and INVENTION EXAMPLES 1 and 2. The results are given in Table 11.

Table 11:

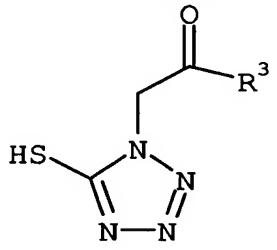
Invention Example nr.	stabilizer type	CIELAB-values of prints with fresh film				Shift in CIELAB-values of prints after 3d/57°C/ 34%RH in dark		Shift of CIELAB-values of prints after 3d/30°C/85%RH light-box exposure		
		D = 1.0		D = 2.0		D = 1.0		D = 1.0		Dmin
		a*	b*	a*	b*	Δa*	Δb*	Δa*	Δb*	Δb*
27	MTA-1	-2.8	-7.8	-0.1	-5.6	-0.1	+3.2	-	-	+2.8
28	Compound 1	-2.5	-6.7	+0.5	-5.2	+0.5	+6.4	-	-	+2.7

The results of Table 11 show that the 1-(5-mercapto-1-tetrazolyl)-acetyl compound, MTA-1 and compound 1 with two groups represented by formula (IV),according to the present invention, upon incorporation into the thermosensitive elements of substantially light-insensitive thermographic recording materials provide stabilization to exposure to light and acceptable image tone when used in combination with S03, benzotriazole.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

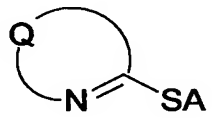
CLAIMS

1. A substantially light-insensitive black and white monosheet thermographic recording material comprising a support and a thermosensitive element, said thermosensitive element containing a substantially light-insensitive organic silver salt, an organic reducing agent therefor in thermal working relationship therewith, a binder and at least one stabilizer selected from the group consisting of 1-phenyl-5-mercaptotetrazole compounds in which said phenyl group is substituted with a substituent containing an optionally substituted aryl group, 1-(5-mercapto-1-tetrazolyl)-acetyl compounds represented by formula (III):



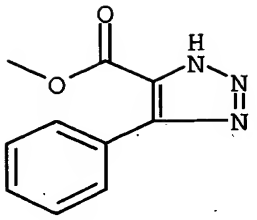
(III)

wherein R^3 is $-NR^4R^5$, $-OR^6$ or an optionally substituted aryl or heteroaryl group; R^4 is hydrogen or an optionally substituted alkyl, aryl or heteroaryl group; R^5 is an optionally substituted aryl or heteroaryl group; and R^6 is an optionally substituted aryl group; compounds with two or more groups represented by formula (IV):



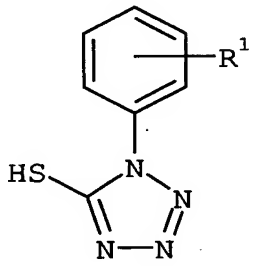
(IV)

where Q comprises the necessary atoms to form a 5- or 6-membered unsaturated heterocyclic ring, A is hydrogen, a counterion to compensate the negative charge of the thiolate group or two or more A groups provide a linking group between the two or more groups represented by formula (IV); 2-mercapto-benzothiazole compounds substituted by an alkyl, an aryl, an alkoxy, a nitro, a cyano or an acyl group or a halogen atom; and



2. Substantially light-insensitive black and white monosheet thermographic recording material according to claim 1, wherein said thermosensitive element further comprises an optionally substituted benzotriazole.

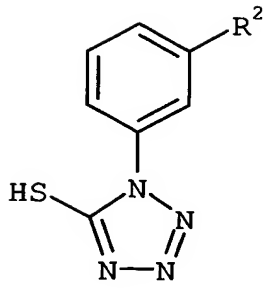
3. Substantially light-insensitive black and white monosheet thermographic recording material according to claim 1 or 2, wherein said 1-phenyl-5-mercaptotetrazole compound in which said phenyl group is substituted with a substituent containing an optionally substituted aryl group is represented by formula (I):



(I)

wherein R^1 is -NH-(C=O)-Ar, -NH-(C=O)-NH-Ar, -NH-(C=O)-O-Ar, -O-(C=O)-NH-Ar, -(C=O)-NH-Ar, -NH-SO_2-Ar, -O-(C=O)-Ar, -O-(C=O)-O-Ar, -(C=O)-Ar, -(C=O)-O-Ar, -SO_2-Ar, -SO_2-NH-Ar, or -Ar; and Ar is an optionally substituted aryl or heteroaryl group.

4. Substantially light-insensitive black and white monosheet thermographic recording material according to claim 1 or 2, wherein said 1-phenyl-5-mercaptotetrazole compound in which said phenyl group is substituted with a substituent containing an optionally substituted aryl group is represented by formula (II):

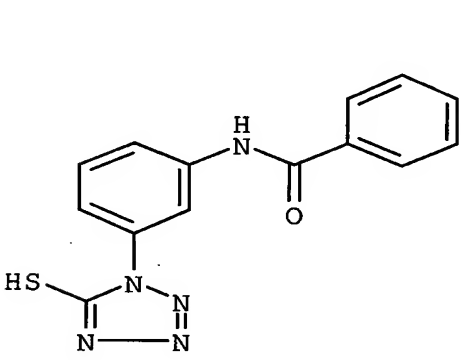


(II)

wherein R^2 is -NH-(C=O)-Ar, -NH-(C=O)-NH-Ar, -NH-(C=O)-O-Ar, -O-(C=O)-NH-Ar, -(C=O)-NH-Ar, -NH-SO_2-Ar, -O-(C=O)-Ar, -O-(C=O)-O-Ar, -(C=O)-Ar, -(C=O)-O-Ar, -SO_2-Ar, -SO_2-NH-Ar, or -Ar; and Ar is an optionally substituted aryl or heteroaryl group.

5. Substantially light-insensitive black and white monosheet thermographic recording material according to claim 1 or 2, wherein at least one of said 5- or 6-membered unsaturated heterocyclic rings is a pyridine, a pyrazine, a pyrimidine, a triazine, a pyrrole, a 1,2,3-triazole, a 1,2,4-triazole, a tetrazole, an oxadiazole, a thiadiazole, an oxazole, an iso-oxazole, a thiazole, an iso-thiazole or an imidazole ring.

6. Substantially light-insensitive black and white monosheet thermographic recording material according any of the preceding claims, wherein said at least stabilizer is selected from the group consisting of:



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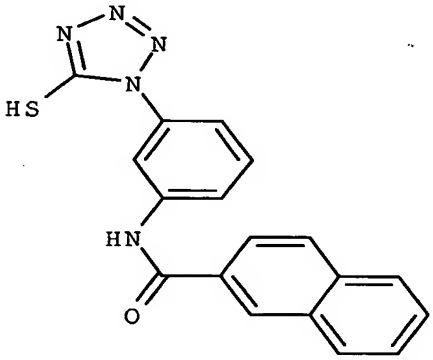

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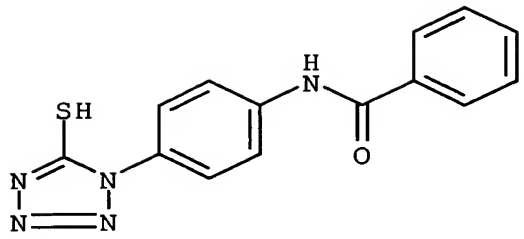

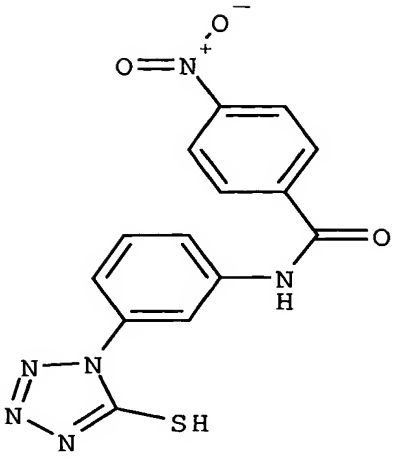

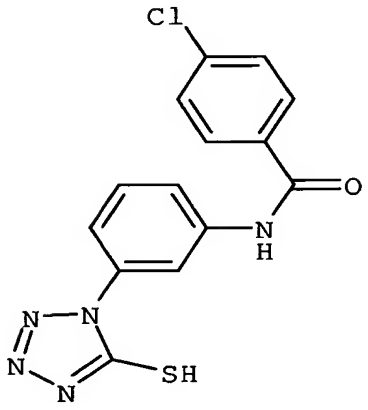

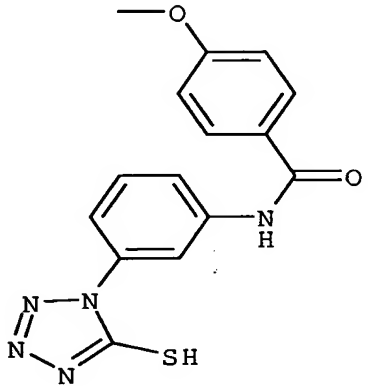

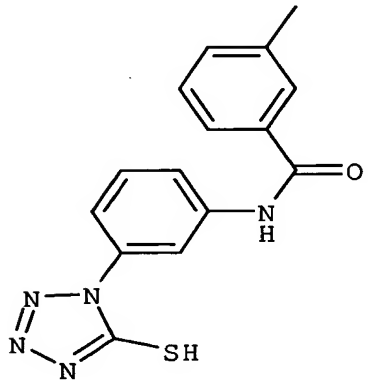

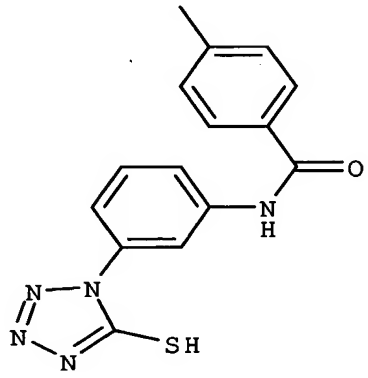

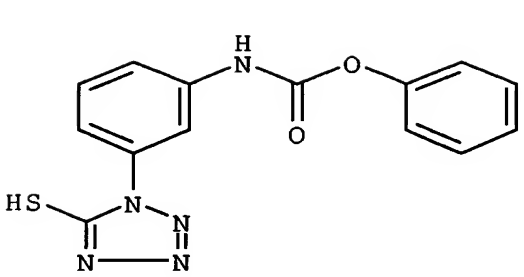

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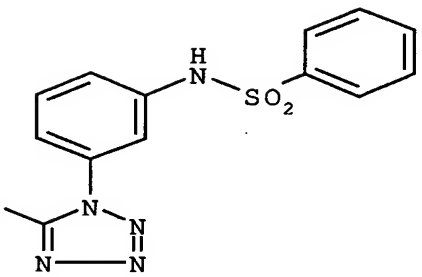

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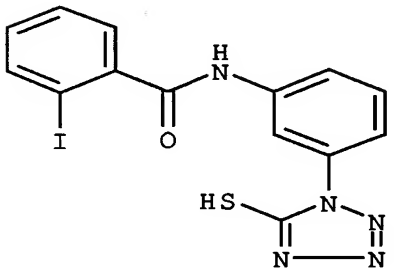

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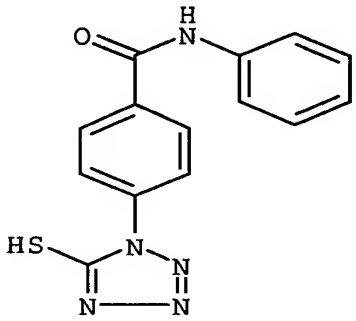
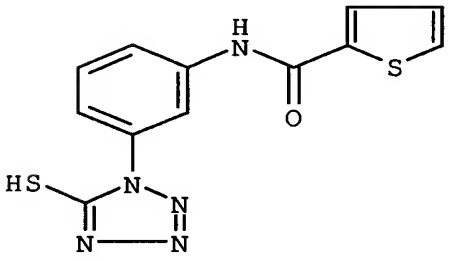


and



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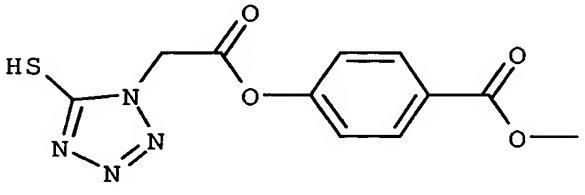
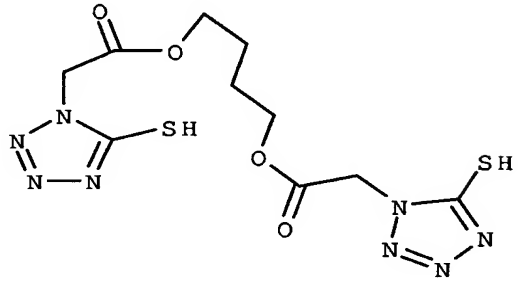
7. Substantially light-insensitive black and white monosheet thermographic recording material according to any of the preceding claims, wherein said at least one stabilizer is selected from the group consisting of:





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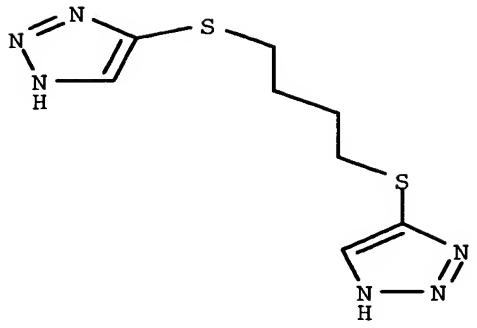
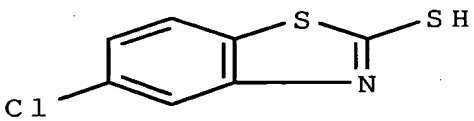
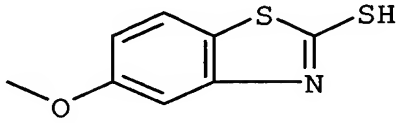


and .

8. Substantially light-insensitive black and white monosheet thermographic recording material according to any of the preceding claims, wherein said at least one stabilizer is



or



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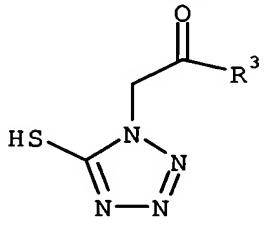
ABSTRACT

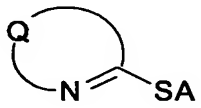
STABILIZERS FOR USE IN SUBSTANTIALLY LIGHT-INSENSITIVE THERMOGRAPHIC RECORDING MATERIALS

A substantially light-insensitive black and white monosheet thermographic recording material comprising a support and a thermosensitive element, the thermosensitive element containing a substantially light-insensitive organic silver salt, an organic reducing agent therefor in thermal working relationship therewith, a binder and at least one stabilizer selected from the group consisting of 1-phenyl-5-mercaptotetrazole compounds in which the phenyl group is substituted with a substituent containing an optionally substituted aryl group, 1-(5-mercapto-1-tetrazolyl)-acetyl compounds represented by formula (III):



(III)

wherein R^3 is $-NR^4R^5$, $-OR^6$ or an optionally substituted aryl or heteroaryl group; R^4 is hydrogen or an optionally substituted alkyl, aryl or heteroaryl group; R^5 is an optionally substituted aryl or heteroaryl group; and R^6 is an optionally substituted aryl group; compounds with two or more groups represented by formula (IV):



(IV)

where Q comprises the necessary atoms to form a 5- or 6-membered unsaturated heterocyclic ring, A is hydrogen, a counterion to compensate the negative charge of the thiolate group or two or more A groups provide a linking group between the two or more groups represented by formula (IV); 2-mercapto-benzothiazole compounds substituted by an alkyl, an aryl, an alkoxy, a nitro, a cyano or an acyl group or a halogen atom; and